

The Influence of Nitrate on Selenium in Irrigated Agricultural Groundwater Systems

Ryan T. Bailey,* William J. Hunter, and Timothy K. Gates

Selenium (Se) contamination of groundwater is an environmental concern especially in areas where aquifer systems are underlain by Se-bearing geologic formations such as marine shale. This study examined the influence of nitrate (NO_3^-) on Se species in irrigated soil and groundwater systems and presents results from field and laboratory studies that further clarify this influence. Inhibition of selenate (SeO_4^{2-}) reduction in the presence of NO_3^- and the oxidation of reduced Se from shale by autotrophic denitrification were investigated. Groundwater sampling from piezometers near an alluvium-shale interface suggests that SeO_4^{2-} present in the groundwater was due in part to autotrophic denitrification. Laboratory shale oxidation batch studies indicate that autotrophic denitrification is a major driver in the release of SeO_4^{2-} and sulfate. Similar findings occurred for a shale oxidation flow-through column study, with 70 and 31% more reduced Se and S mass, respectively, removed from the shale material in the presence of NO_3^- than in its absence. A final laboratory flow-through column test was performed with shallow soil samples to assess the inhibition of SeO_4^{2-} reduction in the presence of NO_3^- , with results suggesting that a concentration of NO_3^- of approximately 5 mg L⁻¹ or greater will diminish the reduction of SeO_4^{2-} . The inclusion of the fate and transport of NO_3^- and dissolved oxygen is imperative when studying or simulating the fate and transport of Se species in soil and groundwater systems.

SELENIUM (Se) occurs naturally as a trace constituent in geologic formations and associated soils and is an essential nutrient for animals and humans, although high concentrations and bioaccumulation can prove detrimental to health. These two effects have led to Se being termed an “essential toxin” (Stolz et al., 2002) and the “double-edged sword” element (Fernández-Martínez and Charlet, 2009), with a narrow range between dietary deficiency (<40 µg d⁻¹) and toxic levels (>400 µg d⁻¹) (Levander and Burk, 2006) for humans. Over the previous three decades, the presence of either deficient or elevated concentrations of Se in ground waters, surface waters, and associated plants and cultivated crops has emerged as a serious issue in the United States (Seiler, 1995; Seiler, 1997; Gates et al., 2009; Hudak, 2010), northern and western Europe (Bye and Lund, 1982; Aro et al., 1998; Alftan et al., 1995), the Middle East (Afzal et al., 2000; Kuisi and Abdel-Fattah, 2010), and East Asia (Mizutani et al., 2001; Zhang et al., 2008). Toxic concentrations in surface water bodies fed by contaminated aquifer systems have led to deformities and death among waterfowl (Flury et al., 1997) and fish populations (Hamilton, 1998; Skorupa, 1998).

Regardless of the nature of concern regarding Se, whether concentrations are at deficient or toxic levels in water supplies and habitats and in cultivated crops, there is a basic need for information on the movement of and chemical processes that influence Se within a dynamic soil-aquifer system influenced by agricultural practices. The transport and transformation of Se species in soil and groundwater systems have been well documented (Fernández-Martínez and Charlet, 2009), with efforts principally guided toward remediation schemes that eliminate Se from the groundwater solution through oxidation-reduction (redox) and sorption processes.

The study of the fate and transport of Se species is incomplete without an understanding of the effects of higher-redox species such as dissolved oxygen (O_2) and nitrate (NO_3^-) on Se. These effects include (i) inhibition of the chemical reduction of toxic forms of Se (Masschelein et al., 1990; Oremland et al., 1989; Weres et al., 1990; Sposito et al., 1991; White et al., 1991; Zhang and Moore, 1997), and (ii) the release of Se from shale due to the autotrophic

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*Corresponding author (rtbailey@engr.colostate.edu).

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5585 Guilford Rd., Madison, WI 53711 USA

R.T. Bailey and T.K. Gates, Dep. of Civil and Environmental Engineering, Colorado State Univ., 1372 Campus Delivery, Fort Collins, CO 80523-1372; W.J. Hunter, USDA-ARS, Suite 100, 2150D Centre Ave., Fort Collins, CO 80526-8119. Mention of manufacturer or product brand name is made for the reader's convenience and does not reflect endorsement by the authors or their sponsors. Assigned to Associate Editor Chad Penn.

Abbreviations: ARS, Agricultural Research Service; BTC, break-through curve; DMSe, dimethyl-selenide; LARB, Lower Arkansas River Basin.

reduction of oxidative species (Wright, 1999; Fernández-Martínez and Charlet, 2009; Stillings and Amacher, 2010).

For the former process, inhibition of reduction allows toxic forms of Se to remain in solution, leading to enhanced leaching and transport to surface water bodies. Studies investigating the fate and transport of Se in soil systems often neglect the influence of O_2 and NO_3^- on Se speciation and transformation (e.g., Guo et al., 1999) and hence predict the reduction and immobilization of Se in agricultural soils when in fact Se would remain in solution and be leached due to the presence of O_2 or NO_3^- . For the process of autotrophic reduction, O_2 -rich or NO_3^- -rich groundwater coming into contact with shale present in the shallow or deep subsurface layers oxidizes reduced Se to mobile forms.

In this report, we present a short review of Se transport and transformations in soil and aquifer systems and examine the influence of NO_3^- on these processes. We also present results from field and laboratory work that lend insight into these influences within an irrigated agricultural groundwater system. Surface soil and bedrock shale samples taken from an irrigated region within the Lower Arkansas River Basin (LARB) in southeastern Colorado were collected for analysis, and piezometers were installed near the alluvium–bedrock shale interface for groundwater sampling. Soil surface samples were used in flow-through column studies to determine the influence of NO_3^- on Se transformations, bedrock shale samples were used to determine the release of Se in O_2^- and NO_3^- -rich water, and groundwater samples from the piezometers were used to determine the in situ relationship between NO_3^- and Se.

Selenium Chemistry and Conceptual Model of Transport in an Irrigated Agricultural Groundwater System

Selenium is present in nature primarily in the four oxidation states of +6 (selenate [SeO_4^{2-}]), +4 (selenite [SeO_3^{2-}]), 0 (elemental selenium [Se^0]), and -2 (selenide [Se^{2-}]). Selenide occurs in many forms, such as the organic selenomethionine (SeMet), the gaseous dimethyl-selenide (DMSe, a product of the volatilization of SeMet), and solid Se found in geologic formations in the form of seleno-pyrite ($FeSe_2$), in which Se substitutes for sulfur (S) in pyrite (FeS_2) (Bye and Lund, 1982) or as other Se-bearing species (Ryser et al., 2005). Soluble species of Se include SeO_4^{2-} (which is one of the most toxic of the Se species), SeO_3^{2-} , and SeMet, whereas Se^0 and other forms of Se^{2-} are insoluble and hence immobile unless suspended. Due to the biogeochemistry of Se and its dependence on redox conditions, Se speciation is largely dependent on local environmental conditions, although SeO_4^{2-} has been reported to account for approximately 90 to 95% of soluble Se in oxygenated agricultural waters (Masscheleyn et al., 1990; Gates et al., 2009). Toxicity of most forms of Se^{2-} is strong, although it has been reported that the toxicity of gaseous DMSe is 500 to 700 times less than that of SeO_4^{2-} (Calderone et al., 1990; Stork et al., 1999).

The movement of soluble Se species in soil and aquifer systems is governed by (i) redox reactions, which control the speciation of Se, and (ii) sorption processes, which retard the advective transport of the species (Fig. 1). Selenate, with the highest oxidation state, is reduced to SeO_3^{2-} , which can be reduced to Se^0 , SeMet, or various selenides, depending on pH. Both processes are mediated by microbial populations (Macy et al., 1989; Oremland et

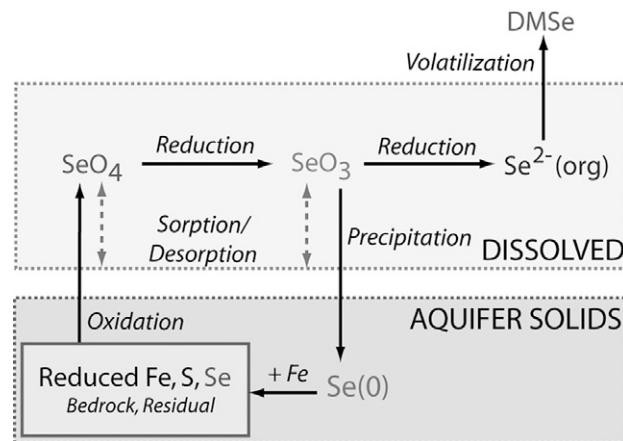
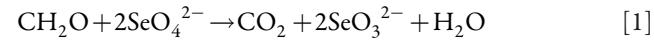
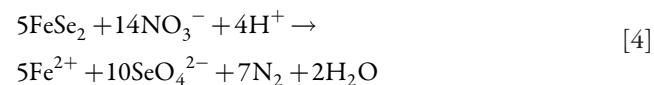
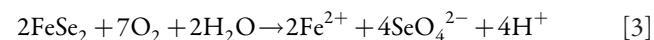


Fig. 1. Oxidation-reduction transformations of Se species in a soil and groundwater system. DMSe, dimethyl-selenide.

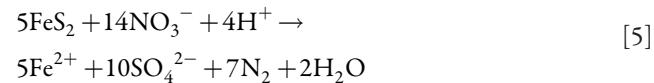
al., 1990; Zhang and Moore, 1997) and are depicted by the following chemical reactions:



where $Se_{(s)}$ and CH_2O represent elemental Se and a generic organic carbon compound, respectively. The requirements for Se reduction to proceed are similar to those listed by Korom (1992) for heterotrophic denitrification and include (i) the presence of microbial populations possessing the appropriate metabolic capacity, (ii) suitable electron (e^-) donors, (iii) the presence of e^- acceptors, which in this case are SeO_4^{2-} or SeO_3^{2-} , and (iv) restricted availability of O_2 . Also, SeO_4^{2-} can be produced through oxidation of residual Se by O_2 or NO_3^- (Fig. 1), for example in the oxidation of $FeSe_2$ within geologic formations:



These reactions are analogous to those in which FeS_2 is oxidized by O_2 or NO_3^- to produce sulfate (SO_4^{2-}) (Frind et al., 1990; Pauwels et al., 1998):



The processes depicted by Eq. [3] and [4] are likely the cause of Se contamination of surface water in regions underlain by marine sedimentary rocks such as shale. The National Irrigation Water Quality Program study, conducted between 1986 and 1993 in 26 irrigated regions within 14 states of the western United States, demonstrated that toxic levels of Se concentration in agricultural drainage waters typically occur when irrigated aquifer systems are underlain by marine shales (Seiler, 1995, 1997).

Methods of removing soluble Se species from environmental waters include (i) reducing SeO_4^{2-} , which sorbs weakly (Ahrlrichs

and Hossner, 1987; Neal and Sposito, 1989) to SeO_3 , which sorbs strongly (Ahlrichs and Hossner, 1987; Balistrieri and Chao, 1987) via the process in Eq. [1]; (ii) reducing SeO_3 to immobile elemental Se⁰, as in Eq. [2]; or (iii) reducing SeO_3 to SeMet, which is then volatilized to DMSe (Calderone et al., 1990; Flury et al., 1997; Frankenberger and Arshad, 2001). Due to the succession of terminal e^- acceptor processes (Korom, 1992; McMahon and Chapelle, 2008), each of these mitigation pathways is inhibited by the presence of higher-redox species such as O_2 and NO_3^- . With O_2 and NO_3^- present in the system, SeO_4^{2-} remains in the dissolved phase and undergoes transport through the groundwater system, although Oremland et al. (1999) observed simultaneous reduction of NO_3^- and SeO_4^{2-} and Oremland et al. (1990) posited a lower “threshold” concentration at which NO_3^- and SeO_4^{2-} reduction can occur simultaneously. This also was suggested by the data presented by Gates et al. (2009), with a NO_3^- concentration of approximately 10 mg L^{-1} (or about 2.3 mg L^{-1} as NO_3^- -N), below which SeO_4^{2-} reduction should proceed.

Hence, in an agricultural groundwater system where O_2 and NO_3^- are present in the subsurface due to infiltrating irrigation water and seepage from earthen canals and NO_3^- is prevalent due to fertilizer and mineralization of crop residue, SeO_4^{2-} entering the aquifer system via irrigation water and canal seepage has a tendency to enter the saturated zone through leaching. Furthermore, leached O_2 and NO_3^- coming into contact with outcropped or bedrock shale liberates additional SeO_4^{2-} into the aquifer through the oxidation of reduced Se, presumably in the form of FeSe_2 or other Se-bearing minerals.

Materials and Methods

Piezometer Installation and Groundwater Sampling

Nine piezometer wells at six locations were installed in June 2009 within the Upstream Study Region (Gates et al., 2009) in southeastern Colorado, a 50,400-ha region that is part of an ongoing extensive investigation of the irrigated stream-aquifer system of the LARB and is located upstream from John Martin Reservoir (Fig. 2). The six locations were situated along a groundwater flow path, from the highest-contour canal—the Rocky Ford Highline Canal—to the Arkansas River, a distance of approximately 7.5 km.

The piezometer wells were installed by Layne Christensen Company using the AP 1000 Percussion Hammer Drill. Upon drilling to the desired depth, 5.08-cm-diameter PVC risers were placed within the borehole with a 1.52-m screen at the base. A filter pack, composed of Colorado silica sand, was placed around the PVC from the base of the borehole to 2 ft above the top of the screen. After predeveloping the well using a surge block and bailer, a 1-m vertical section of bentonite chips was added to the top of the filter pack to act as a primary annular seal, followed by a portland cement secondary annular seal from the top of the bentonite chips to the ground surface. The surface was sealed using concrete and a flush mount manhole cover. The metal casing used to drill the boreholes was decontaminated between each drilling event.

The depth to bedrock at Sites 1, 2, 3, 4, 5, and 6 (see Fig. 2) are 9.8, 12.8, 6.7, 13.7, 15.7, and 12.2 m, respectively. At each site, a

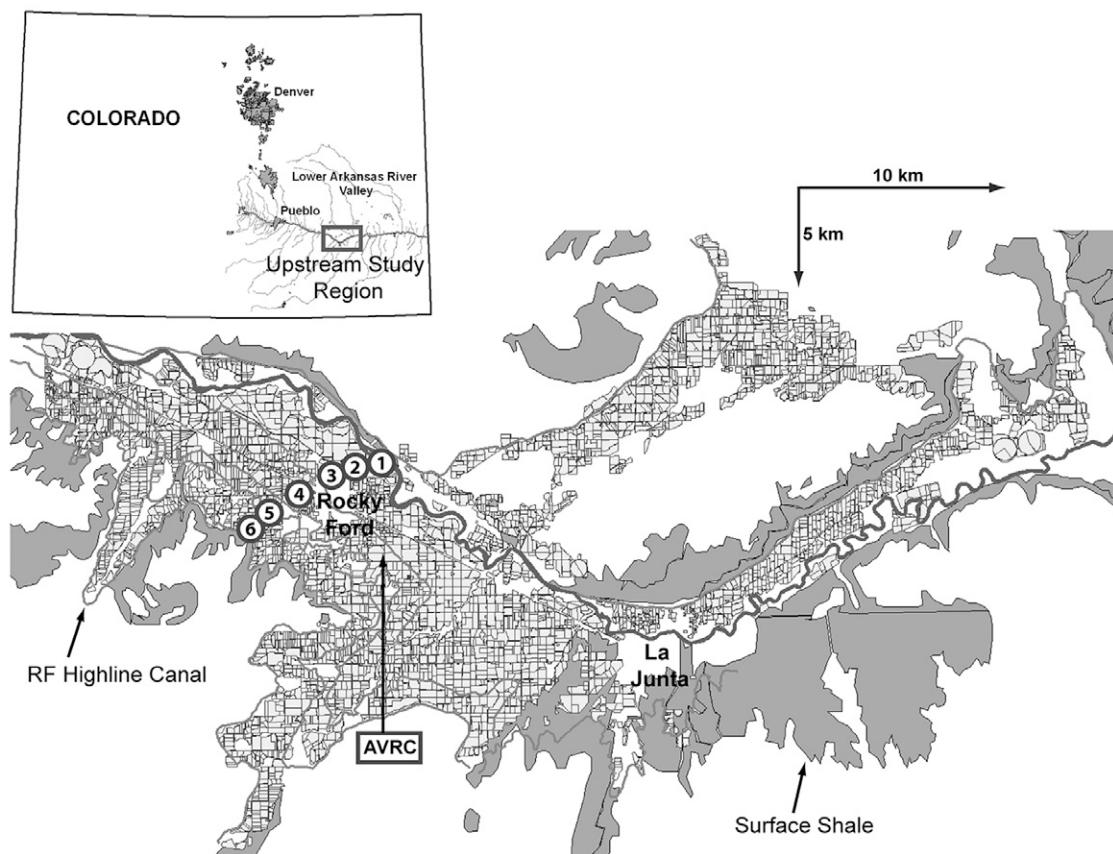


Fig. 2. Upstream study region (Gates et al., 2009) within the Lower Arkansas River Basin in southeastern Colorado showing the locations of the six piezometer placement sites and the Arkansas Valley Research Center (AVRC), where soil was collected for analysis. Surface shale is shaded in gray. The Arkansas River is depicted in a dark gray line, and irrigation canals are depicted in light gray lines. RF, Rocky Ford.

piezometer was installed with the screen positioned just above the alluvium–bedrock interface. At sites 2, 3, and 4, a second adjacent piezometer was installed with the screen positioned at the approximate vertical midpoint between the ground surface and the bedrock. For all sites, a clay loam layer extended from the ground surface to 2.5 to 5.0 m below the ground surface. For sites 1, 2, 3, and 4, gravelly alluvium extended from the base of the clay loam layer to a 0.50- to 0.75-m-thick section of weathered shale atop the shale bedrock, whereas for sites 5 and 6 a tight yellow clay formation extended to the shale.

Groundwater was sampled from each piezometer well during the following sampling events: 25 Aug. 2009, 28 Sept. 2009, 19 Oct. 2009, 29 Dec. 2009, 6 Apr. 2010, 17 June 2010, 8 Sept. 2010, and 1 Dec. 2010. Well purging and groundwater extraction was conducted using a low-flow QED Sample Pro bladder pump (Gates et al., 2009), and samples for NO_3^- and Se were filtered through disposable in-line 0.003-m², 0.45- μm capsule filters. Samples for Se were taken in a 0.12-L plastic (polypropylene or polyethylene) bottle, and samples for NO_3^- were taken in 0.25-L plastic bottles. Samples for Se were preserved at pH <2 by adding \sim 0.005 L of 10% ultrapure nitric acid (HNO_3) in reagent water per liter of sample (\sim 0.00625 L per 0.12-L sample bottle) before sample collection. All samples were stored on ice. Field blanks were taken once per day before sample collection to ensure that sample contamination had not occurred in the field. Field duplicates for groundwater were gathered to assess the field sampling and analytical process.

Samples were analyzed for Se at the Olson Biochemistry Laboratories at South Dakota State University in Brookings, South Dakota (USEPA certified) using Official Methods of Analysis of AOAC International, 17th Edition, test number 996.16 Selenium in Feeds and Premixes, Fluorometric Method. This method determines the concentration of selenite as Se (SeO_3^{2-} –Se). Total recoverable Se is determined by reducing all forms of selenium within the sample to SeO_3^{2-} with hydrochloric acid (HCl). The concentration of SeO_4^{2-} –Se was estimated by subtracting the concentration of SeO_3^{2-} –Se before adding HCl from the concentration of SeO_3^{2-} –Se after adding HCl. The detection limit was $0.4 \mu\text{g L}^{-1}$. Samples for NO_3^- analysis were analyzed by Ward Laboratories, Inc. using the standard USEPA method (method 353.2) (USEPA, 1983).

Shale Analysis and Oxidation Study

Samples of shale were collected from the bottom of the borehole at each of the six sites during the drilling process, placed on ice, and transported to the Agricultural Research Service (ARS) laboratories at the USDA Natural Resources Research Center in Fort Collins, Colorado for storage. Samples were air-dried, ground to a particle size of approximately 0.75 mm, and sent to Olson lab for analysis of Se mass. Selenium mass was determined by predigesting the samples using nitric and perchloric acids, with an aliquot of the predigest analyzed according to AOAC 996.16. Samples for sites 1 through 6 contained mass concentrations ($\mu\text{g g}^{-1}$) of 5.15, 1.04, 2.33, 7.15, 4.70, and 3.77, respectively.

At site 4 (13.7 m depth), in situ samples were collected using a split-spoon sampler, placed on ice, and transported to the ARS laboratories for storage. These samples were used for table-top batch and flow-through column oxidation studies for analysis of the release of SeO_4^{2-} from the shale in the presence of oxygenated

solutions. The release of SO_4^{2-} was also analyzed because oxidation of FeS_2 was expected to occur.

For the batch study, three different buffer solutions were used. The first solution contained O_2 , the second contained a NO_3^- –N concentration of 19.2 mg L⁻¹, and the third was depleted of both. All three solutions were composed of 225 mL of very hard reconstituted water (Greenburg et al., 1992), 4.5 mL of phosphorus stock solution (68 g L⁻¹ of KH_2PO_4), and 200 mL of Hoagland's trace elements (Blankendaal et al., 1972) to preserve the microbial population in the shale samples. The first solution was exposed to the atmosphere to bring the O_2 concentration to equilibrium. For the latter two, the solution was deoxygenated by (i) bringing the solution to a boil; (ii) applying a vacuum for 2 min; (iii) sparging with nitrogen (N_2) gas for 4 to 5 min, with steps (i) through (iii) repeated three times; and (iv) placing the solution in a BBL GasPak 150 anaerobic jar made anaerobic via GasPak pouches (Becton Dickinson Co.) within a N_2 glove bag (Aldrich AtmosBag, Sigma-Aldrich Co.). After 3 d, the solution was transferred to 250-mL bottles within the glove bag, and 7 g of shale sample was added. Bottles were prepared in duplicate.

Sampling from the O_2 , NO_3^- , and control (C_t) bottles was performed immediately upon adding the shale sample to the solution and on Days 1, 2, 4, 8, and 16. Sampling was performed within the glove bag by placing the anaerobic jar inside the glove bag and purging the bag three times with N_2 gas before opening the anaerobic jar. In between sample dates, the anaerobic jar was placed on an Innova incubator orbital shaker (New Brunswick) operated at 28°C and 100 rpm. The NO_3^- and SO_4^{2-} content of the subsamples were measured by suppressed ion chromatography. The analytical system consisted of a Shimadzu LC-10 high-pressure liquid chromatograph, an Alltech DS-Plus auto-suppressor, and a Shimadzu CDD-6 conductivity detector. The elution buffer, pumped at a flow rate of 1 mL min⁻¹, was 0.19 mmol L⁻¹ sodium bicarbonate and 0.55 mmol L⁻¹ sodium carbonate. The analytical column was a 250 by 2.6 mm Serasep AN-1 obtained from Alltech. The remainder of the sample was sent to the Olson lab for analysis of total Se, SeO_3^{2-} –Se, and SeO_4^{2-} –Se using the procedure described previously for groundwater sample analysis.

For the column study, a NO_3^- solution and a de-oxygenated control solution were pumped through columns containing shale samples. The solutions were prepared in the manner described for the batch study. The shale samples were ground, sieved to 1 mm, and homogenized. Forty grams of shale sample were placed in 2.54 by 15 cm glass columns, with a 2.5-cm sand filter on top and bottom of the shale particles to prevent clogging of the influent and effluent tubing. A subsample of the homogenized sample was analyzed separately to determine pre-experiment concentrations. The NO_3^- and C_t solutions, contained in an anaerobic chamber within a glove bag to prevent O_2 contamination, were pumped using a Gilson Minipuls 3 Peristaltic pump through the columns at a rate of 0.8 mL h⁻¹ to simulate slow groundwater flow. Pumping continued for 760 h (31.67 d), after which the shale material within the columns was divided lengthwise into three sections, air-dried, and analyzed for sorbed SeO_4^{2-} –Se, sorbed SeO_3^{2-} –Se, residual Se, and residual S.

For sorption, 10 mL of a 0.1 mol L⁻¹ K_2HPO_4 (9.5 g L⁻¹ of PO_4^{3-}) solution was added to a subsample of the air-dried shale material, with the strong sorbing behavior of PO_4^{3-} assumed to displace sorbed SeO_4^{2-} and SeO_3^{2-} (Fio et al., 1991; Guo et al., 2000).

The solution was placed in a 15-mL centrifuge tube with 1 g of air-dried shale material, shaken on a Burrell wrist-shaker for 24 h, and centrifuged $1620 \times g$ for 15 min. The supernatant was analyzed for total Se, $\text{SeO}_3\text{-Se}$, and $\text{SeO}_4\text{-Se}$ at the Olson lab. Total Se and total S in the dry sample were analyzed at the Olson lab using the methodology described earlier in this section. Residual Se was calculated as the difference between the total Se mass in the dry sample and the combined sorbed $\text{SeO}_3\text{-Se}$ and $\text{SeO}_4\text{-Se}$ mass. The same procedure was performed for the subsample to determine the total mass lost from the shale material.

Nitrate–Selenate Interaction in Shallow Soil

Topsoil was collected from a recently harvested corn plot at the Colorado State University Arkansas Valley Research Center (AVRC) (Fig. 2) in October 2009. The silty clay soil (fine-silty, mixed, calcareous) (Halvorson et al., 2005) was sampled using a hand auger, placed on ice, and transported to the ARS laboratories for storage. The soil was air-dried for 5 d, sieved to between 0.42 and 2.0 mm, and packed into three 2.54 by 15 cm glass columns, with a 2.5-cm sand filter on the top and bottom of the soil. The columns were flushed from below with a 0.05 mol L^{-1} NaCl solution at a flow rate of 0.66 cm h^{-1} for 5 d to displace and remove any soluble and sorbed Se species (Guo et al., 1999). Columns were drained for 10 d, resaturated with the 0.05 mol L^{-1} NaCl solution, and, after verifying that steady-state flow had been achieved, a $\text{NO}_3\text{-SeO}_4$ solution was applied. For all three columns, the influent solution contained $75 \mu\text{mol L}^{-1}$ $\text{SeO}_4\text{-Se}$ (5.92 mg L^{-1} $\text{SeO}_4\text{-Se}$). The solution for the first column contained no NO_3 ; the solution for the second contained $94 \mu\text{mol L}^{-1}$ $\text{NO}_3\text{-N}$ (1.32 mg L^{-1} $\text{NO}_3\text{-N}$ and 5.84 mg L^{-1} NO_3), and the solution for the third contained $800 \mu\text{mol L}^{-1}$ $\text{NO}_3\text{-N}$ (11.2 mg L^{-1} $\text{NO}_3\text{-N}$ and 49.6 mg L^{-1} NO_3). Following Guo et al. (1999), an upflow pumping procedure was used to reduce preferential flow along the column's annular wall.

Effluent from the three columns was collected using a fraction collector (Spectra/Chrom CF1) with collection vials rotated every hour. After 23.5 h of pumping (31 mL of influent solution), the NaCl solution was reapplied to displace NO_3 and the mobile Se species. Pumping was stopped at hour 66 after NO_3 and the mobile Se species had been purged from the top of the column. Nitrate-N, $\text{SeO}_4\text{-Se}$, and $\text{SeO}_3\text{-Se}$ in the effluent were analyzed using the ion chromatograph. After pumping was stopped, the column soils were air dried, and sorbed $\text{SeO}_4\text{-Se}$, sorbed $\text{SeO}_3\text{-Se}$, and residual Se were analyzed using the same procedure as in the shale oxidation column study.

Results and Discussion

Groundwater Sampling

The concentration of $\text{SeO}_4\text{-Se}$ in the groundwater samples from the nine piezometers from the eight sampling events is shown in Fig. 3A in relation to the concentration of $\text{NO}_3\text{-N}$. The correlation between $\text{NO}_3\text{-N}$ and $\text{SeO}_4\text{-Se}$ (log-log) can be seen in Fig. 3A, with higher values of $\text{SeO}_4\text{-Se}$ typically associated with higher values of $\text{NO}_3\text{-N}$. The r^2 value for the log-log relationship is 0.67 (statistically significant at $\alpha = 0.05$). A similar relationship between $\text{NO}_3\text{-N}$ and total dissolved Se (predominantly SeO_4) was found by Wright (1999) for groundwater and surface water samples in areas underlain by shale in western

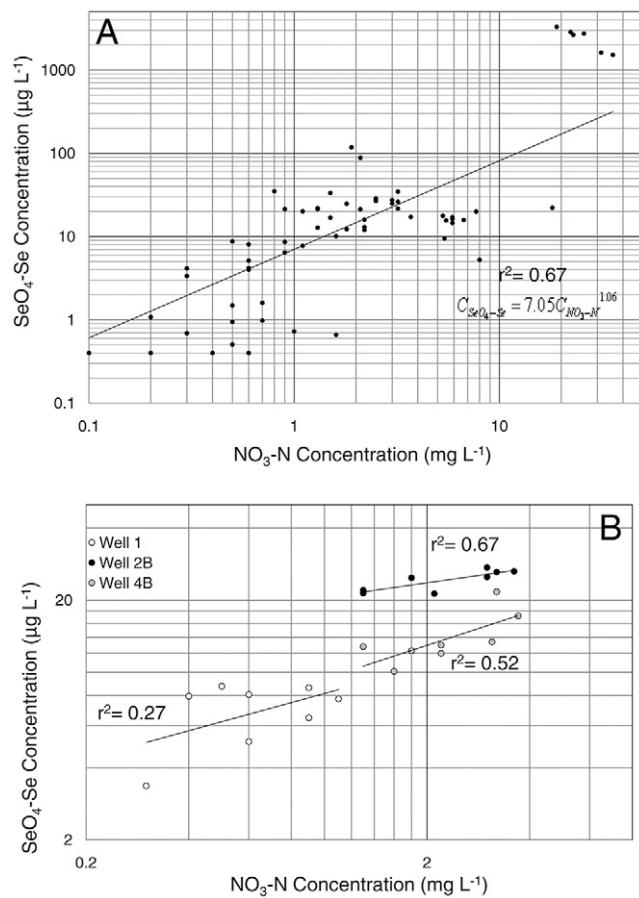


Fig. 3. The concentration of $\text{SeO}_4\text{-Se}$ ($\mu\text{g L}^{-1}$) in groundwater samples from the eight sampling times in relation to the concentration of $\text{NO}_3\text{-N}$ (mg L^{-1}) for (A) all piezometer wells and (B) three piezometer wells located at the alluvium–bedrock shale interface.

Colorado and between NO_3 and total dissolved Se (predominantly SeO_4) by Gates et al. (2009) for the LARB in southeastern Colorado. Concentrations of $\text{SeO}_4\text{-Se}$ and $\text{NO}_3\text{-N}$ were by far the highest in the piezometer at site 6, with average values of $2508 \mu\text{g L}^{-1}$ and 25.9 mg L^{-1} , respectively.

Selenate-Se constituted approximately 93% of soluble Se. Because HNO_3 , a strong oxidizing agent, was used to preserve Se in groundwater samples during shipment, oxidation of SeO_3 to SeO_4 during shipment may have occurred, thus overestimating the in situ SeO_4 groundwater concentration. However, because filtration is assumed to remove the majority of bacterial cells and because samples are stored on ice, any microbial oxidation would proceed at a very low rate. Analysis of field blanks verified that sampling equipment had not been contaminated. Average absolute difference between original and duplicate samples was below 1.4%.

The relationship between $\text{NO}_3\text{-N}$ and $\text{SeO}_4\text{-Se}$ (log-log) is illustrated further in Fig. 3B for individual piezometers (sites 1, 2, and 4) located at the alluvium–bedrock shale interface. Values of r^2 for Well 2B and Well 4B are 0.67 and 0.52, respectively (significant at $\alpha = 0.05$; correlation in Well 1 is not significant), suggesting that the relationship between $\text{NO}_3\text{-N}$ and $\text{SeO}_4\text{-Se}$ is due to autotrophic oxidation of reduced Se (see Eq. [4]). A further indication that this process is not due merely to a general change in groundwater chemistry is seen in Fig. 4A and 4B, which reveal nonsignificant relationships between $\text{NO}_3\text{-N}$ and other groundwater constituents (Na, K, Ca, Mg, CaCO_3 , Cl,

HCO_3^- , B, and SO_4^{2-} -S) at Well 2B and Well 4B, respectively. Although a product of FeS_2 oxidation, the amount of SO_4^{2-} -S released likely is negligible compared with the high background mass of SO_4^{2-} -S in the regional groundwater system (Gates et al., 2009), and hence a significant measurable relationship does not occur between NO_3^- -N and SO_4^{2-} -S.

Shale Oxidation Batch Study

Qualitative Analysis

The batch oxidation study also demonstrates the influence that NO_3^- has on the release of reduced Se from bedrock shale. Figure 5 shows the concentration of SO_4^{2-} -S, SeO_4^{2-} -Se, and SeO_3^- -Se at each of the six sampling times in each of the duplicate O_2 , NO_3^- , and Ct bottles. Dotted lines in Fig. 5 differentiate the duplicates. The production of SO_4^{2-} -S follows an exponential production toward an upper limit, with the O_2 bottles producing more SO_4^{2-} -S (average concentration on Day 16 = 425.5 mg L⁻¹), followed by the NO_3^- bottles (331.3 mg L⁻¹) and the Ct bottles (261.7 mg L⁻¹) (Fig. 5A).

A similar pattern was seen for the production of SeO_4^{2-} -Se (Fig. 5B). After assumed initial dissolution or desorption of SeO_4^{2-} and SeO_3^- from the shale during the first 2 d (see Fig. 5B and 5C), the average concentration of total Se on Day 4 in the O_2 , NO_3^- , and Ct bottles was 32.1, 28.0, and 21.6 $\mu\text{g L}^{-1}$, respectively. Due to the presence of O_2 and the sequence of e^- acceptors, the produced SeO_4^{2-} -Se in the O_2 bottles stayed in solution through the 16 d. During Days 1 through 8, a portion of the dissolved Se was comprised of SeO_3^- -Se (Fig. 5C), which then was sorbed or further

oxidized to SeO_4^{2-} -Se by Day 16. After Day 2, the dissolved Se in the Ct bottles was reduced because there were no inhibiting e^- acceptors present in the solution, although contamination of O_2 into the first Ct bottle seemed to occur between Days 2 and 4. This is evidenced by (i) a high value of SeO_4^{2-} -Se on Day 4 for the first Ct bottle (Fig. 5B), (ii) the large scatter between the Se values on Day 4 (Fig. 5B and 5C) and Day 8 (Fig. 5C) for the two Ct bottles (Fig. 5B and 5C), and (iii) the presence of SeO_4^{2-} -Se in the first Ct bottle on Day 8, when SeO_4^{2-} -Se in the other Ct bottle, as well as the two NO_3^- bottles, had been completely depleted.

Within the NO_3^- bottles, production of SeO_4^{2-} and SeO_3^- was followed by reduction. The sequence of reduction is further elucidated in Fig. 6A and 6B, which show the concentration of NO_3^- -N (mg L⁻¹) and the Se species ($\mu\text{g L}^{-1}$) in both of the NO_3^- bottles for each of the sampling times. On Day 16, NO_3^- , SeO_4^{2-} -Se, and SeO_3^- -Se all had a concentration of 0 in both bottles. The following sequence of events is assumed to have occurred for both bottles: (i) between Days 0 and 2, NO_3^- -N concentration was steady, with any SeO_3^- and SeO_4^{2-} in solution due to dissolution

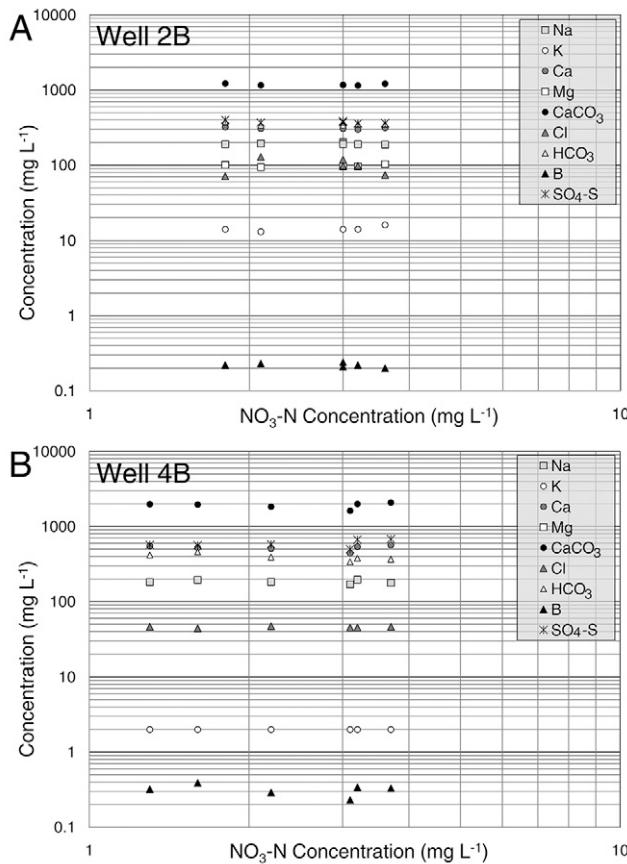


Fig. 4. The concentration of NO_3^- -N (mg L⁻¹) in groundwater samples in relation to other groundwater constituents for (A) Well 2B and (B) Well 4B at the alluvium–bedrock shale interface.

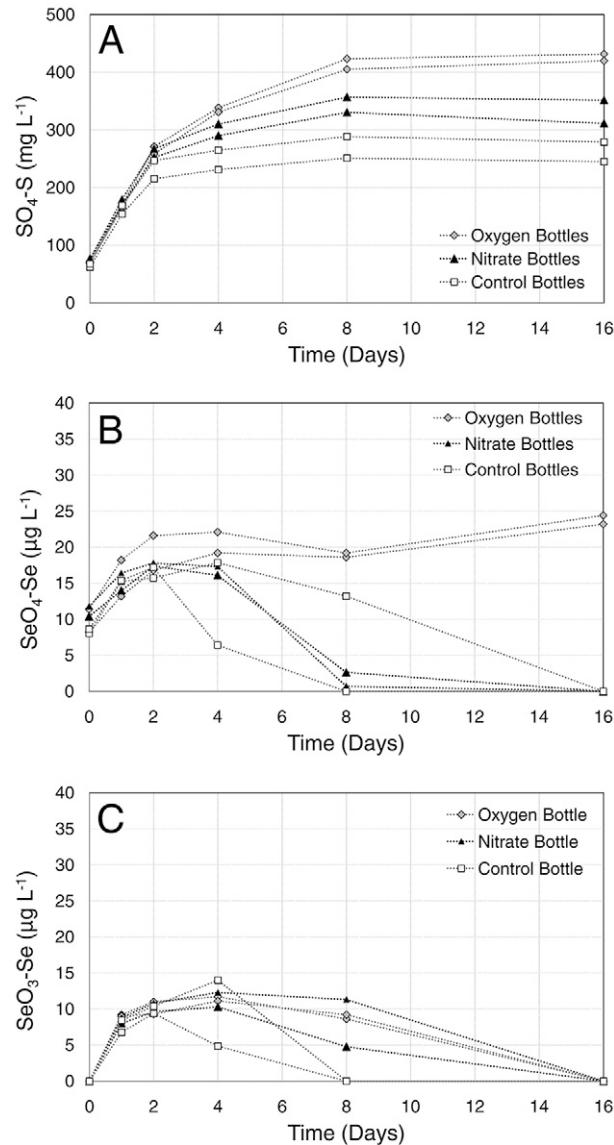


Fig. 5. Concentration of (A) SO_4^{2-} -S, (B) SeO_4^{2-} -Se, and (C) SeO_3^- -Se at sampling times during the shale oxidation batch study in the O_2 solution, NO_3^- solution, and control (Ct) bottles.

from the shale. (ii) Between Days 2 and 4 NO_3^- , as the dominant e^- acceptor, begins to be reduced. However, the NO_3^- -N concentration was still high enough that SeO_4^{2-} was not yet influenced. (iii) Between Days 4 and 8, NO_3^- was depleted, and the NO_3^- -N concentration became low enough for SeO_4^{2-} reduction to commence. This was further evidenced by the production of SeO_3^- -Se, which on Day 8 makes up all of the dissolved Se. (v) Between Days 8 and 16, with NO_3^- and SeO_4^{2-} depleted, SeO_3^- became the dominant e^- acceptor until it was depleted by Day 16 (Fig. 5C). Sulfate was no longer produced (Fig. 5A) after NO_3^- had been depleted. (vi) Between Days 8 and 16, with NO_3^- and SeO_4^{2-} depleted and with SeO_3^- depleted sometime between Days 8 and 16, SO_4^{2-} became the dominant e^- acceptor and began to deplete by Day 16 in the NO_3^- bottles (Fig. 5A).

Overall, the preservation of SeO_4^{2-} in solution until the concentration of NO_3^- dropped to a low value, the depletion of SeO_3^- once the concentration of SeO_4^{2-} dropped to a low value, and the small depletion of SO_4^{2-} between Days 8 and 16 (9.5 and 3.4% average decrease in the C_t and NO_3^- bottles, respectively) are indicators of the process of sequential reduction of e^- acceptors. The inclusion of PO_4^{3-} , a strong competitor with SeO_4^{2-} and SeO_3^- for surface sorption sites, in the P stock solution used in solution preparation may have prevented SeO_4^{2-} and SeO_3^- sorption from occurring, thereby providing an enhanced dissolved concentration. Because SeO_4^{2-} is a weak sorbent, this primarily would affect SeO_3^- . However, the PO_4^{3-} concentration in the solution is approximately one tenth the generally accepted concentration used to displace SeO_4^{2-} and SeO_3^- in laboratory studies (see previous sections). Furthermore, SeO_3^- experiences a steady decline in

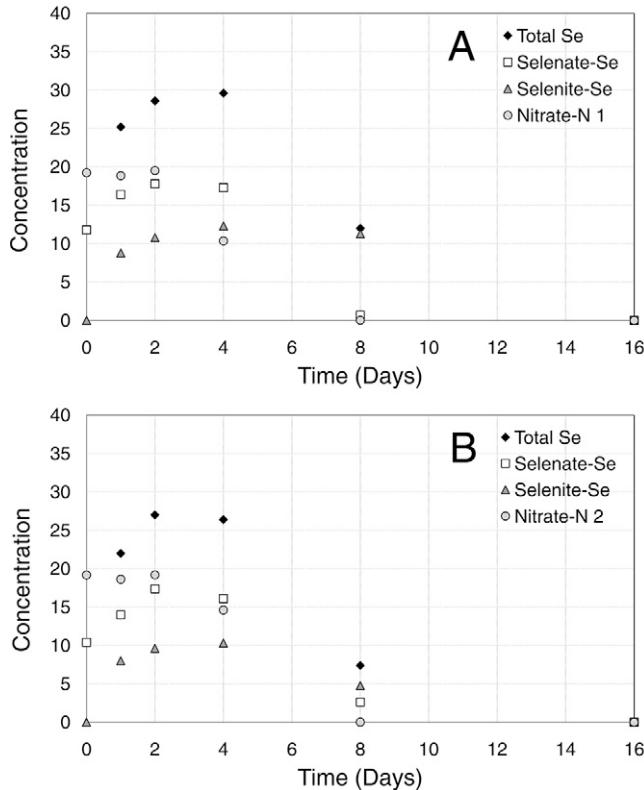


Fig. 6. Concentration of total Se, SeO_4^{2-} -Se, SeO_3^{2-} -Se, and NO_3^- -N in (A) the first NO_3^- solution bottle and (B) the second NO_3^- solution bottle. Concentrations of NO_3^- -N are in mg L^{-1} ; concentrations for Se species are in $\mu\text{g L}^{-1}$.

concentration (Fig. 5C), which is indicative of reduction kinetics. Therefore, the influence of PO_4^{3-} probably is not considerable.

Quantitative Analysis

Using a first-order reaction kinetic model in the differential and associated integrated forms of $dC_i/dt = -kC_i$ and $C_i(t) = C_i(t_0)e^{-kt}$, respectively, the first-order rate constant k [d^{-1}] is estimated for the production of SO_4^{2-} -S, the production of SeO_4^{2-} -Se, and the depletion of NO_3^- . The variable C_i denotes the concentration of constituent i under consideration.

For the production of SO_4^{2-} -S, which corresponds to the chemical reaction represented in Eq. [5], average values of k are 0.054, 0.062, and 0.082 d^{-1} for the C_t , NO_3^- , and O_2 bottles, respectively. For the autotrophic reduction of NO_3^- , the value of k , termed k_{auto} , was 0.157 d^{-1} for the first NO_3^- solution bottle and 0.067 d^{-1} for the second bottle. This corresponds to Eq. [5] because the mass of NO_3^- reduced according to the oxidation of FeSe_2 represented in Eq. [4] is negligible in comparison. These values are shown in Fig. 7A in relation to estimated values of k_{auto} from other denitrification studies (Frind et al., 1990; Pauwels et al., 1998; McMahon et al., 1999).

The reduction of NO_3^- occurs only between Days 2 and 8 (Fig. 6A and 6B); thus, the production of SO_4^{2-} -S due to autotrophic denitrification only occurred during the same time period. This is further confirmed through a stoichiometric mass balance between the mass of N consumed and the mass of S produced,

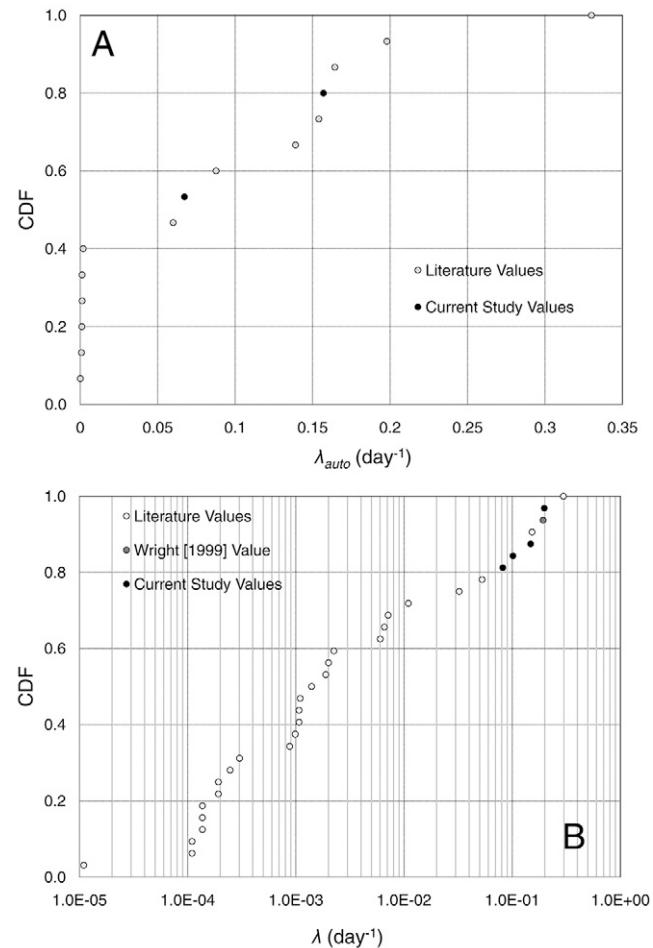


Fig. 7. Empirical cumulative distributive function (CDF) for first-order rate constants for (A) autotrophic denitrification and (B) Se oxidation. Rates estimated during this study are shown in black.

according to Eq. [5]. According to Eq. [5], the ratio of S produced to N consumed is equal to 1.64 (320.65 g/196.0 g). For the first NO_3 bottle, the mass of N depleted is equal to 4.40 mg, whereas the mass of S produced between Days 2 and 8 is 6.76 mg, resulting in an S:N ratio of 1.54. For the second NO_3 bottle, the S:N ratio is 1.24, for an average of 1.39. Hence, the calculated values of λ for SO_4^{2-} -S production encompass presumably initial nonoxidative dissolution of the shale as well as the oxidation of FeS_2 . If only the data points from Days 2, 4, and 8 are used to calculate λ , then the resulting average values of λ are 0.025, 0.045, and 0.072 d^{-1} for the Ct , NO_3 , and O_2 bottles, respectively.

For the production of SeO_4^{2-} -Se, and taking only the first three data points during which production occurred, the average values of λ were 0.092 and 0.173 d^{-1} for the NO_3 and O_2 bottles, respectively. These are similar to the value of 0.193 d^{-1} calculated using the first four data points from the $\text{NO}_3 = 100 \text{ mg L}^{-1}$ bottles in the study performed by Wright (1999). These values are shown in Fig. 7B in relation to estimated values of λ from other Se oxidation studies (Zawislanski and Zavarin, 1996; Losi and Frankenberger, 1998; Dowdle and Oremland, 1998; Stillings and Amacher, 2010). Computed rates are within the range reported in the published literature, although on the higher end.

Shale Oxidation Column Study

Table 1 contains the components of Se mass (sorbed Se, residual Se) in the shale material before and after the solution was pumped through the column to determine the mass of reduced Se that was released from the shale material during the experiment. The first column in Table 1 is the total Se mass concentration ($\mu\text{g g}^{-1}$) in each section of the NO_3 and Ct columns; the second and third columns contain the mass concentration of sorbed SeO_3^{2-} -Se and sorbed SeO_4^{2-} -Se, respectively, and the fourth column contains the mass concentration of the residual Se, calculated as the difference between the total Se and the sorbed Se. The fifth column is total reduced Se mass in each section (μg), column six is the total reduced Se mass for the entire shale column, and the last column shows the mass of reduced Se that was lost during the 760 h of solution pumping through a comparison of the final and initial reduced Se mass.

The majority of the initially sorbed SeO_3^{2-} -Se and SeO_4^{2-} -Se mass (total = $0.64 \mu\text{g g}^{-1}$) was displaced. Also, 69.8% more reduced Se mass was removed in the NO_3 column ($24.31 \mu\text{g}$ removed) than in the Ct column ($14.33 \mu\text{g}$ removed). The effect of oxidation by NO_3 also can be seen through an analysis of the

reduced S mass (Table 2). In the NO_3 column, 0.18 g of reduced S mass was removed from the shale column, compared with 0.13 g from the Ct column, for a difference of 30.9%. A decrease in reduced Se and S mass in the Ct column is likely due to some type of nonoxidative dissolution or to contamination of the influent solution with O_2 and subsequent O_2 autotrophic reduction and Se oxidation according to Eq. [3].

Shallow Soil Column Study

The break-through curve (BTC) of SeO_4^{2-} -Se in the effluent for each of the three soil columns, using the normalized value of $C_{\text{SeO}_4}/(C_{\text{SeO}_4})_0$, is shown in Fig. 8, along with the BTC for NO_3 in the third column (initial $C_{\text{NO}_3-\text{N}} = 11.2 \text{ mg L}^{-1}$). The NO_3 in the second column (initial $C_{\text{NO}_3-\text{N}} = 1.32 \text{ mg L}^{-1}$) was depleted before leaving the soil column. Table 3 contains the percentage of the total Se mass introduced into the column for each mass balance component (effluent, sorbed Se, reduced Se) for the three columns. The italicized cells in Table 3 correspond to components of Se mass that are a result of SeO_4^{2-} reduction, following the pathways of (i) SeO_4^{2-} reduction to SeO_3^{2-} , followed by sorption of SeO_3^{2-} , and (ii) SeO_4^{2-} reduction to SeO_3^{2-} , which was then reduced to residual Se.

In Table 3, the mass of SeO_4^{2-} -Se leaving the soil column in the effluent, in relation to the mass of SeO_4^{2-} -Se entering the column in the influent, is least for column 1 (33.2%), followed by column 2 (43.3%) and then by column 3 (75.5%). This is reflected in the areas under the BTC of SeO_4^{2-} -Se for each column (Fig. 8). Most importantly, the mass of reduced Se in relation to the mass of SeO_4^{2-} -Se entering the column in the influent is much higher for column 1 (30.6%), where NO_3 is absent, than for column 2 (8.1%) and column 3 (5.0%). Furthermore, the mass of SeO_4^{2-} -Se reduction products (sorbed SeO_3^{2-} -Se + reduced Se) accounts for 32.6% of the influent Se mass in column 1, followed by only 10.6% for column 2 and 6.1% for column 3. Even though the influent NO_3-N concentration for column 2 was approximately one-tenth the influent NO_3-N concentration for column 3, the percentage of influent SeO_4^{2-} -Se mass that was reduced is only slightly increased, indicating the inhibition of SeO_4^{2-} reduction in the presence of NO_3 . With the percentage of reduced Se mass slightly higher for column 2 than for column 3, the threshold NO_3-N concentration at which the microbial population jointly reduced NO_3 and SeO_4^{2-} may be posited above 1.32 mg L^{-1} (5.84 mg L^{-1} NO_3). This result is in general agreement with the

Table 1. Components of Se mass in the shale column sections, demonstrating the loss of mass in the shale material during the flow-through column experiment.

Section	Total Se	Sorbed SeO_3^{2-} -Se	Sorbed SeO_4^{2-} -Se	Reduced Se	Reduced Se	Total reduced Se	Total reduced Se lost
$\mu\text{g g}^{-1}$							
Initial mass							
All	5.08	0.29	0.35	4.45	177.92	177.92	-
Final mass							
NO_3 top	3.64	0.08	0.11	3.45	46.02		
NO_3 middle	4.41	0.07	0.09	4.25	56.68	153.61	24.31
NO_3 bottom	4.07	0.10	0.15	3.82	50.92		
Ct top	4.27	0.09	0.13	4.05	54.00		
Ct middle	4.84	0.09	0.11	4.65	61.96	163.59	14.33
Ct bottom	3.74	0.06	0.10	3.57	47.64		

Table 2. Comparison of reduced sulfur mass in the shale columns before and after the solution pumping.

Section	Total S μg g ⁻¹	Total S μg	Total S g	Mass lost
Initial mass				
All	11,780	471,200	0.47	—
Final mass				
NO ₃ top	6,265	83,533		
NO ₃ middle	8,080	107,733	0.29	0.18
NO ₃ bottom	7,580	101,067		
Ct top	8,623	114,973		
Ct middle	9,432	125,760	0.34	0.13
Ct bottom	7,040	93,867		

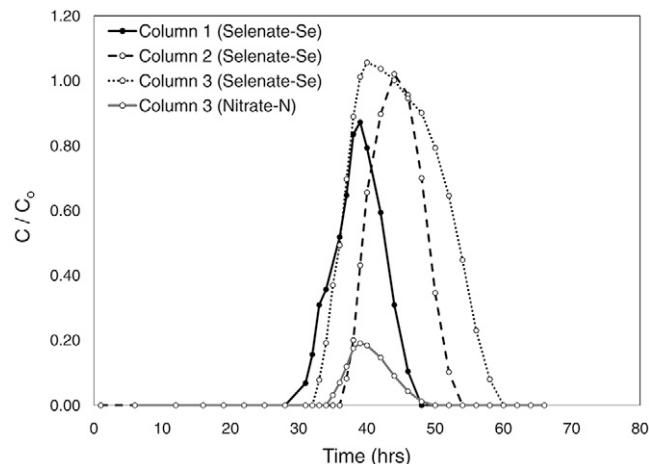


Fig. 8. Break-through curves for SeO₄-Se for the three soil columns and the break-through curve for NO₃-N for the third soil column (influent NO₃-N concentration = 11.2 mg L⁻¹).

groundwater sampling data and analysis presented by Gates et al. (2009) for the LARB.

The stronger capacity for SeO₄ reduction exhibited in column 1 is further demonstrated in Fig. 9, which shows the mass of reduced Se in the top, middle, and bottom sections of the three columns. For each section, the reduced Se mass is much less for columns 2 and 3 than for column 1. For column 3, there is no residual Se in the bottom section of the column because the high NO₃-N concentration prevents the reduction of the incoming SeO₄. However, as the solution migrates upward through the soil column, NO₃ was reduced and was eventually lowered to a concentration at which SeO₄ also was reduced. Hence, the reduced Se mass in the middle and top sections for column 3 were similar to that in column 2.

Conclusions

Field groundwater sampling and laboratory experiments conducted in this study have strengthened the premise that oxidative

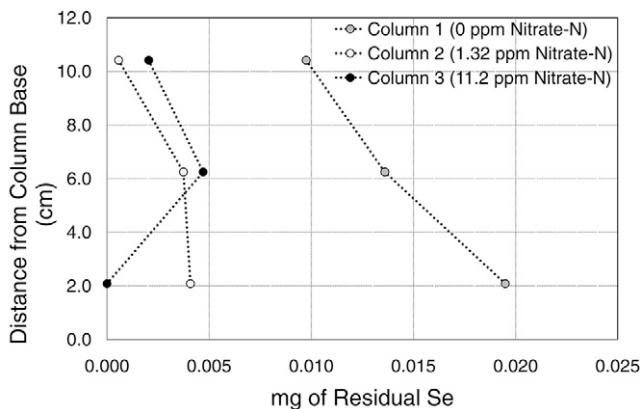


Fig. 9. Mass of reduced Se in the top, middle, and bottom sections of the three columns in the NO₃-SeO₄ soil column study.

species such as NO₃ have a significant influence on the fate and transport of Se species in soil and groundwater systems. Results show that under high-redox conditions, represented in this study by the presence of NO₃, SeO₄ can be released from Se-bearing shale and can be kept in solution through inhibition of chemical reduction to SeO₃, hence inhibiting mitigation of Se contamination.

Failure to account for the presence of O₂ and NO₃ in Se subsurface fate and transport studies may result in an overall nonconservative and harmful approach because such studies overestimate the rate of SeO₄ reduction in soil and groundwater systems and neglect the introduction of SeO₄ into the groundwater system through oxidation of reduced Se species present in shale and other geologic formations. This is especially important in irrigated agricultural areas, where NO₃ is present in abundance due to the application of inorganic and organic N fertilizers and the recharging flows that result from excess irrigation application and canal seepage. Furthermore, some strategies currently being used to mitigate NO₃ contamination itself, such as autotrophic denitrification in the presence of shale, may exacerbate the Se contamination problem for a given aquifer system. These strategies must be reconciled, which almost certainly must include reducing fertilizer application using optimized management strategies that maintain acceptable crop yield. Because an accurate depiction of the fate and transport of NO₃ in soil and groundwater systems generally requires an accounting of various components of the N cycle, the inclusion of NO₃ in Se fate and transport studies is not a trivial undertaking. However, accurate results and interventions for successful mitigation generally will be reached only when this is performed.

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Table 3. Percentage of the total influent mass of selenium attributed to each mass balance component.

Column	NO ₃ -N mg L ⁻¹	Percentage of total influent mass of Se (mg)						
		Total Se in mg	Effluent SeO ₄ -Se	Effluent SeO ₃ -Se	Sorbed SeO ₄ -Se	Sorbed SeO ₃ -Se	Reduced Se	Total
Column 1	0.0	0.14	33.2	0.0	27.6	2.0†	30.6	93.5
Column 2	1.32	0.10	43.3	0.0	32.1	2.5	8.1	86.0
Column 3	11.2	0.14	75.5	0.0	27.1	1.1	5.0	108.7

† Italics indicate product from the reduction of SeO₄.

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